Polarization memory decay spectroscopy of photoexcitations in π-conjugated polymers: Evidence for excimers

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We used the technique of ultrafast transient polarized photomodulation in the visible/near-infrared range and polarization memory decay (PMD) spectroscopy to study the primary photoexcitations in films and solutions of two poly(phenylene-vinylene) (PPV) derivatives, namely, 2-methoxy-5-(2′-ethylhexyloxy) PPV (MEH-PPV) and 2,5-dioctyloxy PPV (DOO-PPV). We found that the primary photoexcitations in DOO-PPV films and solutions and MEH-PPV solutions are *intrachain singlet excitons* that show the same PMD across the entire spectrum. In contrast, the ultrafast photoexcitations in MEH-PPV films are of two kinds; these are intrachain excitons with fast PMD kinetics and *interchain species* with very slow PMD kinetics, which is the property that identifies these photoexcitations as *excimers (or interchain charge transfer exciton)*. We attribute the excimers in MEH-PPV films to the increased interchain coupling due to the tightly packed nanomorphology, which also explains the photoluminescence efficiency decrease and its odd kinetics.

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In the last two decades, π-conjugated polymers have been used as active layers in a variety of optoelectronic devices such as light emitting diodes, solar cells, photodetectors, lasers, and light emitting field-effect transistors.[1–4] Among the variety of π-conjugated polymers, poly(phenylene-vinylene) (PPV) and its soluble derivatives have shown a high photoluminescence (PL) quantum efficiency, and therefore, these polymers have been excellent candidates for active layers in electroluminescence devices. From the application point of view, their photophysics is crucial, and hence, the PPV derivatives have been the subject matter of a large body of experimental and theoretical research studies.[5–9] In spite of these efforts, there has still been an intense debate on the nature of the primary photoexcitations in these polymers. There is a consensus that the primary photoexcitations in PPV derivative polymers in *dilute solutions* are intrachain singlet excitons.[10] However, in *films* of PPV derivatives, species other than intrachain excitons may also be instantaneously photogenerated[9] due to the increased interchain coupling. Some of these latter species discussed in literature are polaron pairs, excimers, and free polarons.[5–10] These various photoexcitations have associated signature optical transitions, and thus, their identification in the transient photomodulation (PM) spectra has been attempted based on their characteristic below-gap photoinduced absorption (PA) bands.[9,10] Among the various instantaneously generated photoexcitations, however, only the intrachain exciton has been unambiguously identified due to the correlation of its characteristic PA bands with a stimulated emission (SE) band in the PM spectrum.[8,10] However, the other interchain species have always been hotly debated due to their intimate relation with the interchain interaction strength in the films, which substantially varies depending on the nature of side groups, solvent, and processing conditions used for the film fabrication, as well as different intensity of the pump laser excitation.[11–13]

Recently, an elegant theoretical investigation was completed,[14] in which the eigenstates of two coupled polymer chains that have interchain interactions of various strengths were calculated. The basic Hamiltonian used in the calculation included intrachain and interchain transfer integrals ($t_{\|}$ and $t_{\perp}$, respectively), as well as electron-electron and electron-hole interactions that were taken into account in a realistic way. Based on these calculations, it was concluded that the lowest excited state of the *coupled chains* is an *excimer* or *interchain charge transfer exciton*,[15] wherein the charge ionicity f on the two coupled chains varies in the range $0<f<1$. There are also states of polaron pair character with $f=1$ and intrachain excitons with $f=0$, but these states lie *above* the lowest excimer state. The excimer characteristic PA bands were also calculated.[14] Although the emphasis in that work was mainly on the lowest energy PA band, which actually redshifts with respect to the PA band of the intrachain exciton, PA_1, a higher energy PA band was also anticipated for the excimer species at energy higher than that of PA_1. It thus experimentally remains unsettled whether excimers are indeed photogenerated in real polymer films.

Due to the quasi-one-dimensional nature of the π-conjugated polymer chains, most photoexcitation-related characteristic PA bands show an anisotropic polarization behavior, which can be measured by the technique of polarization memory decay (PMD) kinetics $P(t)$.[16] In our earlier work on ultrafast transient PM spectroscopy of various π-conjugated polymers,[9] we found a relationship between the lifetime τ_P of the photoexcitations PMD and the interchain coupling strength of the polymer chains in the film; namely, the larger the ratio of $t_{\perp}/t_{\|}$ is, the smaller τ_P is. Furthermore, the PMD kinetics technique may be an ideal tool to discern between the various photoexcitation species in polymer films. We expect fast PMD kinetics for intrachain excitons and free polarons since these species are very mobile among the polymer chains in the film. However, the excimer and polaron-pair species should be more localized in places along the chains where the interchain distance between neighboring chains is the smallest, and consequently, their binding energy (mainly Coulombic in nature) is the largest, and this increases their stability. Of the two types of interchain photoexcitations, however, the excimer is the least

mobile specie since it is a quantum state based on the *interchain transfer integral* in addition to the Coulomb binding, and thus, it is more sensitive to the interchain distance.[17] Therefore, very slow PMD kinetics characterizes the excimer species.

In this work, we report the transient PM spectra in the visible/near-infrared range from 1.25 to 2.55 eV, and PMD of various PA bands in the PM spectrum in films and solutions of two PPV derivatives, namely, 2-methoxy-5-(2′-ethylhexyloxy) PPV (MEH-PPV) and 2,5-dioctyloxy PPV (DOO-PPV). We found that DOO-PPV solutions and films and MEH-PPV solution mainly support *singlet excitons* as primary photoexcitations since there is a *single* PA band in the PM spectrum that is well correlated with the SE band and P(t) lifetime does not change across the PM spectrum. In contrast, MEH-PPV films support *two kinds of ultrafast photoexcitations*. These are (i) intrachain excitons with the same characteristic properties as excitons in DOO-PPV and (ii) interchain species that we identify as *excimers* with larger initial P(0) and *much slower PMD kinetics*. We also found that the relatively strong interchain coupling in MEH-PPV films influences the PL quantum efficiency and its decay, wherein most of the steady state PL comes from a long-lived component.[18,19]

For the transient PM measurements, we used an amplified Ti:sapphire laser system with pulses of ~150 fs duration at 1.55 eV, at a repetition rate of 1 kHz.[9] The fundamental laser beam was frequency doubled to 3.1 eV and was used as a pump beam with a photon energy above the polymers optical gap. The probe beam was white light "supercontinuum" in the spectral (or frequency) range of 1.25–2.55 eV, which was generated by passing a portion of the fundamental laser beam through a 1 mm thick sapphire crystal plate. The probe pulses were mechanically delayed with respect to the pump pulses by a computer-controlled translation stage. To achieve tight spatial alignment of the pump and probe beams on the sample, the pump beam was focused to 1 mm diameter spot on the film, whereas the probe beam was focused to 0.4 mm diameter at the center of the pump beam spot. The unavoidable spectral chirp in the probe supercontinuum beam was taken into account by using a "chirp-free" compensating program that controls the translation-stage "zero time" at $t=0$ ps for different probe frequencies. We measured the differential transmission ($\Delta T/T$) of the probe beam due to the modulated pump beam by using a phase sensitive technique locked to the pump beam modulation frequency at ~500 Hz. For the PMD measurements, the linear polarization of the probe beam was adjusted to be either parallel ($\parallel$) or perpendicular ($\perp$) to the pump beam polarization by using a quarter-wave plate; we measured both $(\Delta T/T)_{\parallel}$ and $(\Delta T/T)_{\perp}$, respectively, for the parallel and perpendicular pump-probe polarizations. The P(t) was then calculated by using the expression $P(t)=[(\Delta T/T)_{\parallel}-(\Delta T/T)_{\perp}]/[(\Delta T/T)_{\parallel}+(\Delta T/T)_{\perp}]$.[9] The PL quantum efficiency (QE) of the polymer films and solutions was measured by using an integrated sphere, wherein the absorption, reflectivity, and scattering of the excitation beam on the sample were separately evaluated and then taken into account for the QE calculation.

DOO-PPV was synthesized in house,[20] whereas MEH-PPV powder was bought from American Dye Corp. Both polymers were dissolved in toluene with a concentration of 0.1 mg/ml for the solutions and 5 mg/ml for the films. The polymer films were drop cast from the solution and subsequently dried at 50 °C for 1 h in vacuum to remove any solvent left. The measurements of the solution were done at ambient, whereas for the films, the measurements were conducted under dynamic vacuum of 10^{-5} Torr to prevent fast photo-oxidation.

Figure 1(a) shows the transient PM spectrum of the DOO-PPV film at $t=0$ ps along with the steady state cw PL and absorption spectra for comparison. The PL spectrum contains two bands with peaks at 2.1 eV (0–0) and 1.95 eV (0–1), wherein the lower energy band (0–1) is a phonon sideband of the main band (0–0). The transient PM spectrum shows a single PA band (PA_1) that peaks below 1.25 eV [at ~1.0 eV (Refs. 8 and 9)], and SE in the spectral range between 1.7 and 2.3 eV, which is in fact almost a mirror image of the cw PL spectrum.[10] The transient PM spectrum also shows photobleaching (PB) in the absorption spectral range of the polymer, which is generated in the ground state absorption due to the photoexcitations.

Figure 1(b) shows the PMD kinetics of the DOO-PPV film at three probe frequencies that are related to various spectral features in the PM spectrum; these are 1.35 eV (PA_1), 1.6 eV (~zero-crossing), and 2.0 eV (SE). The polarization memory initial value $P(0)$ and kinetics are roughly the same for all three probe frequencies, with short and long exponential components that have lifetimes of $\tau_P \sim 7$ and ~70 ps, respectively (Table I). Moreover, the PM decay kinetics shown in Fig. 1(c) are also roughly the same at the three probe frequencies with two-component decay lifetimes $\tau_{PA} \sim 7$ and ~90 ps (Table I). This indicates that the PM spectrum results from a *single* excited specie. Since the SE band decay is correlated with that of PA_1 band, we conclude that the primary photoexcitations in MEH-PPV films are *intrachain singlet excitons*. Also, we obtained very similar results (except for τ) in DOO-PPV in solution (Table I). From the PA decay dynamics and the known exciton radiative lifetime $\tau_r \sim 1$ ns in PPV derivatives,[21] we calculated the PL QE efficiency $\eta(=\tau_{SE}/\tau_r)$ of DOO-PPV in film and the solutions 22% and 8%, respectively (Table I). The calculated QE is, in fact, verified by the actual QE obtained by using an integrated sphere (Table I). This shows that the same species are photogenerated in films and solutions, where the lower QE in the films is probably because a nonradiative channel, such as impurities and defects into which the excitons may fall, becomes operative due to the faster exciton diffusion among the polymer chains in the films.

Figure 2(a) shows the transient PM spectrum of MEH-PPV toluene *solution* at $t=0$ ps, along with the cw PL and absorption spectra. The PL spectrum shows two peaks at 2.21 eV (0-0) and 2.09 eV (0-1), respectively. The transient PM spectrum is similar to that in the DOO-PPV film and solution having a single PA band PA_1 that peaks below 1.24 eV and is also similar to SE but slightly blueshifted with respect to the cw PL spectrum. Figure 2(b) shows the PMD kinetics at three probe frequencies of 1.35, 1.66, and 2.12 eV, which have the same $P(0)$ value and lifetime, $\tau_P > 300$ ps (Table I). τ_P value here is longer than those in DOO-PPV films but close to that in DOO-PPV solution (Table I). From

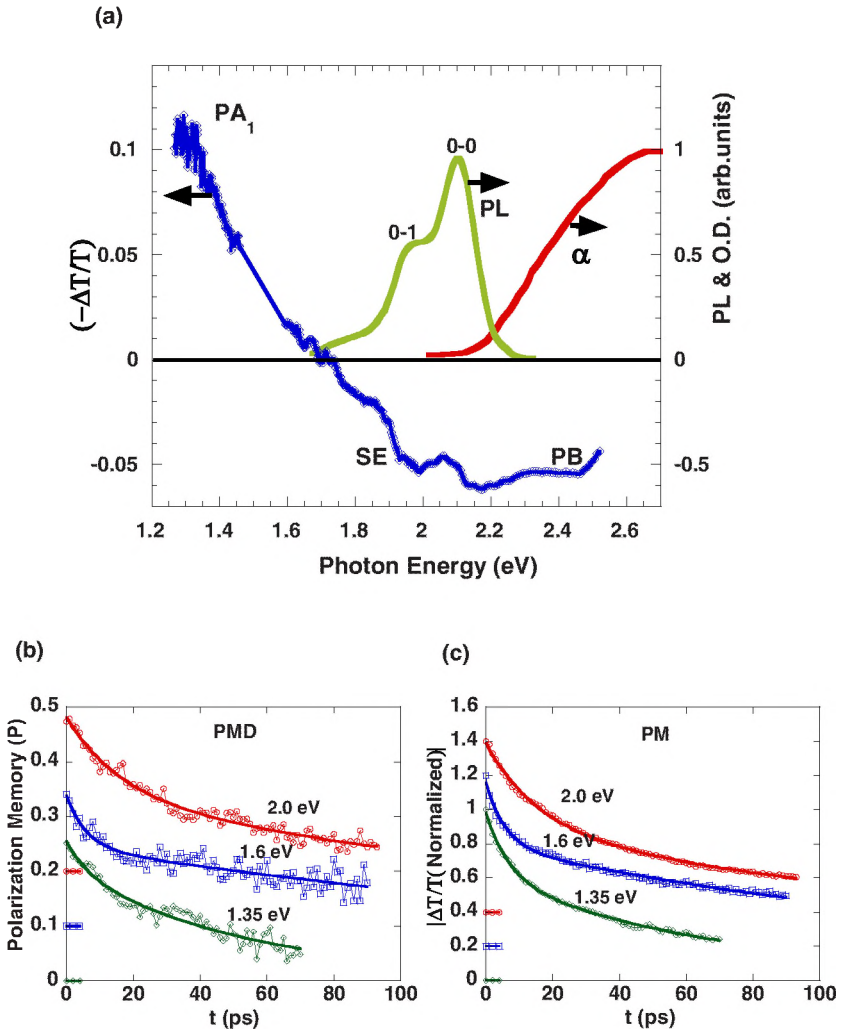


FIG. 1. (Color online) (a) Transient photomodulation spectrum of the DOO-PPV film at $t=0$ ps (left axis); various bands such as PA_1, SE, and PB are assigned. The cw PL with 0–0 and 0–1 phonon replica and absorption spectra are also shown (right axis). (b) PMD and (c) PA kinetics at probe energies of 1.35 (PA_1) (green, diamonds), 1.6 (zero crossing) (blue, squares), and 2.0 eV (SE) (red, circles). The continuous lines are guides to the eye, and for ease of comparison, the various decays are vertically shifted along with their zero value.

TABLE I. The photophysics parameters of the DOO-PPV and MEH-PPV solutions and films. The measured and calculated steady state PL QE, the PM and PMD lifetimes, τ at various probe frequencies in the transient PM spectra. P(0) is the PMD value at $t=0$. The short component lifetime is given as needed for few samples and photon frequencies.

Sample	PL QE (meas.) (%)	PL QE (calc.) (%)	Probe frequency (eV)	Initial PMD [P(0)]	PM lifetime: τ_{PA1}, τ_{PA2} (ps)	PMD lifetime: τ_{P1}, τ_{P2} (ps)
DOO-PPV solution	22	21	1.98	0.27	209	232
			1.66	0.25	221	373
			1.38	0.23	212	590
DOO-PPV film	8	8	2.0	0.28	83	13; 67
			1.6	0.24	118	6; 130
			1.35	0.25	74	7; 56
MEH-PPV solution	24	23	2.12	0.20	233	557
			1.66	0.24	213	344
			1.33	0.15	157	310
MEH-PPV film	12	1	2.0	0.13	10	3
			1.66	0.16	3; 333	3; 540
			1.33	0.09	15	2

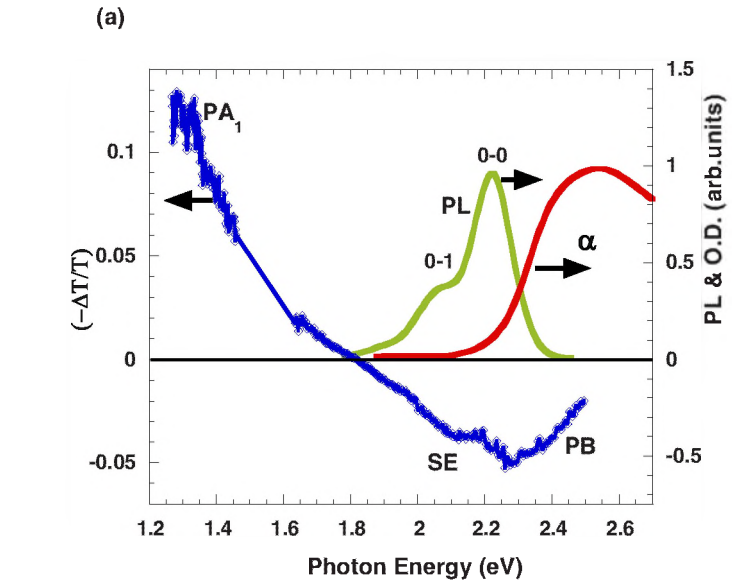
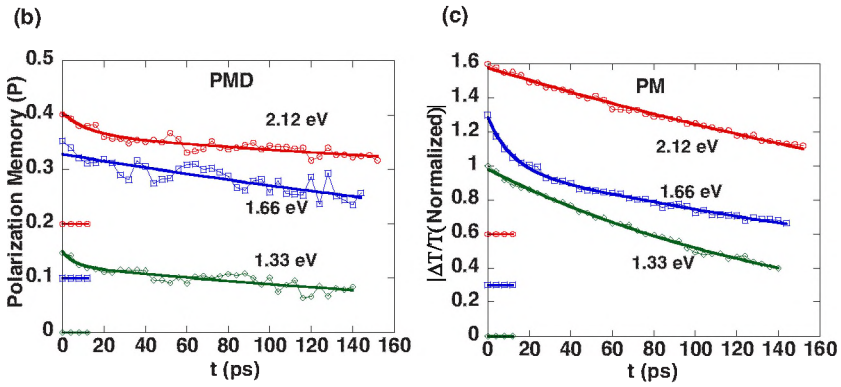


FIG. 2. (Color online) Same as in Fig. 1 but for the MEH-PPV solution.



the decay kinetics of the SE spectrum, we obtained $\tau_{SE} \sim 230$ ps for the exciton lifetime and calculate for the PL efficiency[21] $\eta \sim 23\%$, which is again in good agreement with the measured QE (Table I). As in the DOO-PPV film above, a similar conclusion can be drawn for the MEH-PPV solution; namely, that intrachain *excitons* are the primary photoexcitations, with similar properties as the excitons in DOO-PPV.

Figure 3(a) shows the transient PM spectrum of MEH-PPV *film* at $t=0$ along with the steady state PL and absorption spectra. The cw PL spectrum here is much broader than the spectra in DOO-PPV and MEH-PPV solutions but still shows two emission bands at 2.13 and 2.0 eV, respectively. However, the transient PM spectrum in this film shows very different characteristic properties compared to those in DOO-PPV film and MEH-PPV solution (Figs. 1 and 2, respectively). First, the cw PL is substantially more redshifted here relative to the two peaks in the $t=0$ SE(0) spectrum (peaks at 2.25 and 2.05 eV, respectively). The larger cw PL redshift with respect to SE(0) may originate from two different causes: (i) Much faster exciton migration to lower energy sites exists in MEH-PPV films because the interchain coupling (that helps exciton diffusion among the polymer chains) here is stronger.[8] (ii) There is a lower state (excimer) that is formed for the most strongly coupled chains in the film, into which the original intrachain excitons fall.[14] This would substantially delay the PL emission from this sample; we indeed measured a long PL decay component in MEH-PPV films extending into the microsecond time domain.[22] We favor the latter scenario because fast PMD kinetics is not always accompanied by a substantial PL redshift with respect to SE(0), as the case in the DOO-PPV film discussed above. So, the substantial mismatch between the cw PL and SE(0) obtained in MEH-PPV is truly unique, and this requires a novel explanation.

Second, in addition to the PA_1 and SE bands, there is another PA band in the PM spectrum of the MEH-PPV film, namely, PA_{ex} at ~ 1.65 eV, which shows very different dynamics compared to that of PA_1 and SE. We directly compare the decay dynamics of PA_{ex}, SE, and PA_1 by plotting the PM spectrum at $t=0$ and 60 ps, respectively [Fig. 3(a)]. It is apparent that PA_{ex} kinetics is much slower than that of PA_1 and SE; this is more clearly shown in Fig. 3(c) and summarized in Table I. Third, the PMD kinetics is not the same across the PM spectrum in MEH-PPV film. Figure 3(b) shows the PMD kinetics at three probe frequencies that correspond to the various spectral features in the PM spectrum, namely, 1.33 eV (PA_1), 1.66 eV (PA_{ex}), and 2.0 eV (SE). Whereas $P(t)$ decays very fast within the PA_1 and SE bands with $\tau_P \sim 3$ ps (Table I), it is *much slower* for the PA_{ex} band to decay, where it hardly decays up to $t=80$ ps. Similar to the other polymer samples discussed above, we identify PA_1

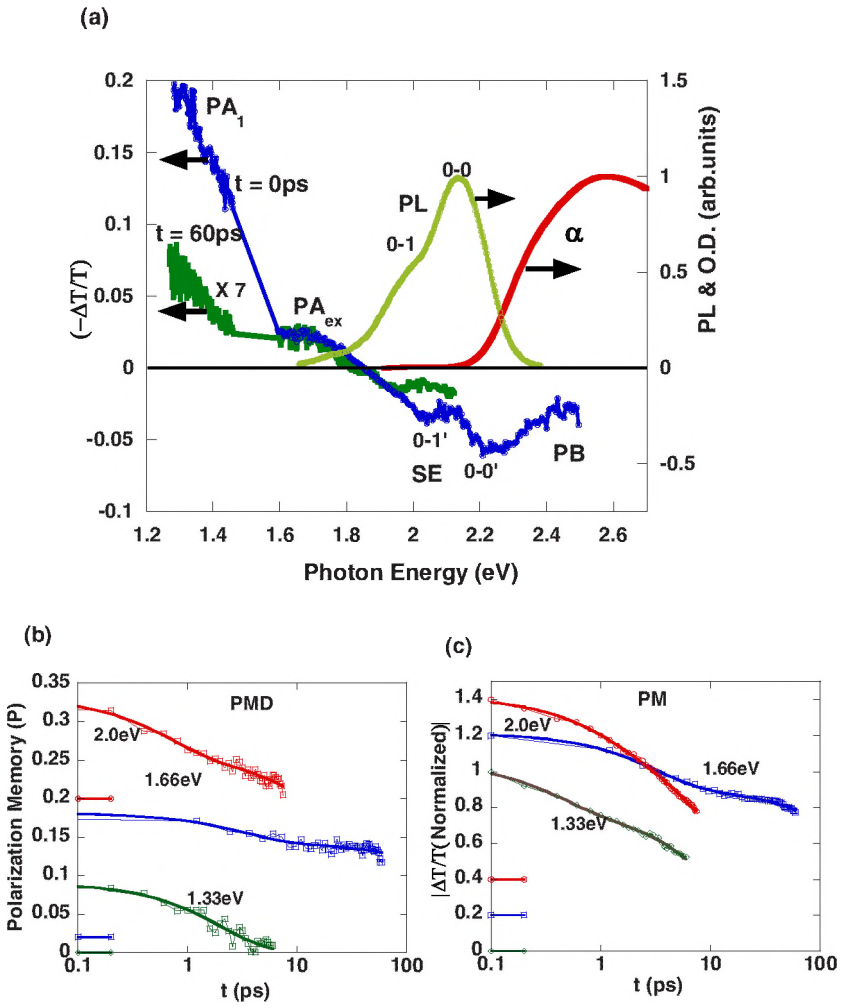


FIG. 3. (Color online) Same as in Figs. 1 and 2 but for the MEH-PPV film at $t=0$ and 60 ps, respectively. In (a) the new PA_{ex} is assigned. In (b) [(c)], the PMD (PA) kinetics is plotted in logarithmical time scale.

and its correlated SE in the MEH-PPV film as due to the intrachain singlet excitons. Then, from the $P(t)$ dynamics for PA_1 and SE, we conclude that exciton diffusion in the MEH-PPV film is very fast ($\tau_P \sim 3$ ps) relative to that in the DOO-PPV film ($\tau_P \sim 60$ ps), which is consistent with the increased interchain coupling in the former sample. In contrast, $P(t)$ at 1.66 eV [Fig. 3(b)] first shows a fast decay within 10 ps, which is probably due to the $P(t)$ decay of the excitons component at this probe frequency, which rides on a very slow component ($\tau_P > 100$ ps). Also, PA_{ex} decay is not correlated with that of SE and, thus, does not have as strong a dipole coupling to the ground state. Taken together, these indicate that PA_{ex} is not related to the intrachain excitons; instead, it belongs to a different photoexcitation specie, which is not as mobile or as strongly coupled to the ground state. Yan *et al.*[12] reported such a band with a peak at ~1.5 eV in another PPV derivative and identified it to be due to interchain polaron pairs. This original interpretation, however, should be modified in favor of excimer since it disagrees with the redshifted cw PL band compared with SE(0) band, as discussed above, and also explains the obtained slow PMD kinetics of these excitations.

Another indication that species other than the intrachain excitons dominantly contribute to the cw PL in the MEH-PPV film is the PL QE. Assuming the same radiative lifetime as that of intrachain excitons [namely, $\tau_r \sim 1$ ns (Ref. 20)], we calculate from PA_1 and SE lifetimes (~10 ps, Table I) the PL QE ($=\tau_{SE}/\tau_r$) of ~1% in MEH-PPV films. In contrast, we measured the PL QE of ~12% for this film, and this relatively large QE cannot originate from intrachain excitons, which decay very fast. We thus conclude that the same long-lived specie that is associated with PA_{ex} may also radiatively recombine at a later time and, thus, also contribute to the PL, as indeed measured in our laboratory.[22] This interchain specie has a *much longer radiative lifetime* compared to that of the intrachain exciton, which might be tracked back to its weaker dipole moment. We therefore identify this interchain specie as an *excimer* (or interchain charge transfer exciton), which is a quantum superposition state of a polaron pair and an interchain exciton, and is also relatively immobile on the chains. The fact that these interchain species appear in ~150 fs, which is our time resolution, does not necessarily show that they are the "primary photoexcitations" of the "coupled chains," since they may be created by hot intrachain excitons that dissociate onto different chains during the excess energy relaxation process. However, a recent theoretical work on coupled chains shows[14] that the excimers are the primary photoexcitations of such coupled chain system indeed; thus, we doubt that measurements at time shorter than our time resolution, say, with a 10 fs resolution,[23] would reveal a buildup of the interchain species.

In summary, we investigated the photoexcited species that contribute to the ultrafast transient PM spectrum in the visible/near infrared range in DOO-PPV and MEH-PPV films and solution by using transient PM and a new spectroscopic technique, namely, PMD kinetics spectroscopy. We show that the primary photoexcitations in the MEH-PPV solution and DOO-PPV film and solution are exclusively singlet excitons with a large SE band. However, the ultrafast PM spectrum in the MEH-PPV *film* contains another PA band at ~1.65 eV, which shows a much slower PA and PMD kinetics compared to those of the intrachain excitons. We identify the underlying species as *excimers* (or *interchain charge transfer excitons*), which also explains the obtained cw PL redshifted spectrum compared to SE(0) spectrum and the relatively high PL QE in spite of the fast PA decay kinetics of intrachain excitons in these films. Our results also show that PMD spectroscopy is a powerful tool for discerning various photoexcitations in the PM spectrum of π-conjugated polymers.

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